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Integrated Solid-State Film Lithium Battery

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Abstract

The several materials required for fabrication of thin-film solid-state rechargeable lithium batteries were deposited and characterized: A glassy lithium-phosphorus oxynitride electrolyte (LiPON) between a lithium (Li) anode and crystalline lithium-cobalt oxide cathode ($LiCoO_2$), deposited by RF-sputtering. Ti/Pt layers, deposited by e-beam were used in contacts and a silicon nitride film (Si_3N_4), deposited by low temperature hot-wire CVD protects the battery. This technology allows batteries with a potential of 4.5 V, typical capacities of 50 μAcm-2 and charge-discharge rates up to 4C. Solid-state film batteries show faster charge rates and very high cycle life, compared with film polymer batteries, withstanding several thousands of cycles with no pronounced fading.

Keywords:Recherageable lithium-battery; LiCoO, LiPON; Sputtering; Energy harvesting

1. Introduction

The increasing energy demand of battery-powered wireless devices requires new energy-scavenging systems, capable of harvesting energy from environment when available and delivers it when necessary. Energy scavenging is mainly based on thermoelectric, vibration and photovoltaic energy sources. However, these generators require backup batteries to provide power when main energy source is not available. Moreover, the battery integration with solid state electronics [1-3] provide a broaden applications area. There is also a great interest in size reduction of batteries due it integration with portable microsystems for biomedical microsystems and application in wireless neural electrodes is intended [4].

Two forms of rechargeable film batteries have been investigated so far: polymer-based lithium batteries and solid-state film lithium batteries. Polymer batteries (that are already common in the market) have high capacity and stability but low charge/discharge rates, mainly due to temperature limits. Solid-state film batteries show faster charge rates and very high cycle life, compared with classical liquid electrolyte batteries, withstanding several thousands of cycles with no pronounced fading. The integration of batteries with solid-state circuits requires the use of solid-state anode and cathode, with solid electrolyte, as presented in this work. These batteries are intrinsically safe, since all materials are solid and no leaking or explosion could occur. Moreover, this technology allows the fabrication of batteries that are not damaged during the soldering process of chips.

A fast ion transfer and incorporation can be obtained if the contact area of anode and cathode is increased. Most attempts to improve the design of batteries have tackled the problem at the macroscopic scale, but work is now

focusing on the nanoscale [1, 5]. Nanostructures were slow to enter the field of energy storage because the effective increase in the electrodes' surface area raised the risk of secondary reactions involving electrolyte decomposition. The arrival of nanostructures gave batteries a new lease of life and provided benefits in terms of capacity, power, cost and materials sustainability that are still far from being fully exploited.

The film battery chemistry is being developed at ORNL [2, 6] with a solid electrolyte between the anode and cathode. These batteries have a potential of 4.5 V, typical capacities below 100 uA/cm^2 and charge times of 2C to 5C. Film batteries have the highest volumetric energy density (800 Wh/l) and gravimetric energy density (350 Wh/g) and charge-discharge rates up to 5C (only exceeded by super-capacitors) [6,7]. However, due to film deposition processes, thickness is limited to few µm, resulting in a small capacity. The film battery market is in the trial stage and it's predictable to reach 10 billion units by 2012.

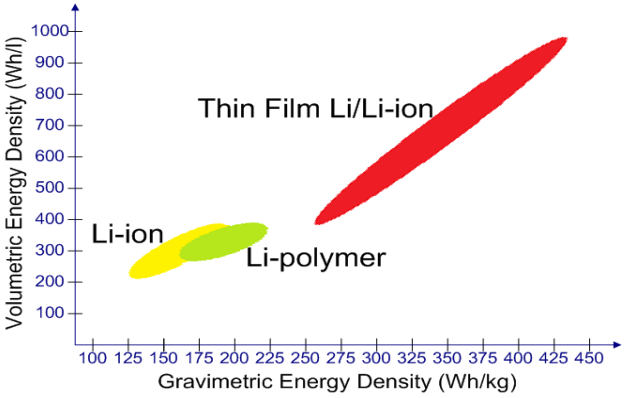

Fig 1: Gravimetric energy density and volumetric energy density of typical lithium batteries.

2. Experimental

The proposed battery is presented in Fig. 2. On top of the substrate ([100] undoped double-side polished Si wafer), a current collector, 30 nm of titanium (Ti) and 100 nm of platinum (Pt), was deposited by e-beam. Pt allows the distribution of electrons trough the cathode surface without reacting with it and Ti is used to improve adhesion of Pt. The cathode is a lithium-cobalt oxide ($LiCoO_2$) film; electrolyte is a glassy lithium-phosphorus oxynitride electrolyte (LiPON) film and anode is a Lithium (Li) film.

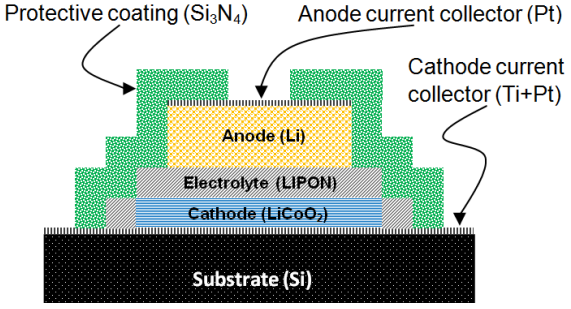

Fig. 2: Artwork of the proposed battery, with $LiCoO_2$ cathode, LiPON electrolyte and Li anode, between Pt contacts, covered by a protective Si_3N_4 film. The thickness of each layer is not on scale for better visualization.

The platinum top anode current collector, with 100 nm thick was also deposited by e-beam. The protection layer, Si_3N_4 film, is then deposited by low-temperature CVD [8]. The use of shadow masks allows the fabrication of structure presented in Fig. 2.

The $LiCoO_2$ is the cathode material due to its excellent electrochemical cycling stability. The 1 µm thick $LiCoO_2$ cathode was deposited by RF magnetron sputtering technique (a RF power source 13.56 MHz at 150 W, a pressure of 0.2 Pa in a 30 sccm flow of Ar and 10 sccm flow of O_2). Despite previous work to avoid annealing temperature

[9] this process is still the most effective way to provide the required crystalline structure of $LiCoO_2$ films. The best annealing temperature was found experimentally using three different temperatures (873 K, 973 K and 1023 K), during 30 min. in vacuum.

The LiPON film was deposited by RF magnetron sputtering technique (1 μm thick). A Li_3PO_4 target was used in a 20 sccm reactive nitrogen flow. The power source (13.56 MHz) was biased at 200 W and three different pressures were tested (1Pa, 0.7 Pa and 0.3 Pa, as presented in Table 1).

The anode of the battery (Li) was deposited by thermal evaporation, using molybdenum boats (3 cm^3 volume).

3. Results

X-ray diffraction measurements (XRD) and SEM images were performed in cathode materials (Fig. 3). After annealing, $LiCoO_2$ films exhibited polycrystalline structure with strong orientation in the (104) planes and fewer at (003) and (101) planes. The in-plane resistivity of 0.2 Om was measured in films annealed at temperature below 1000 K and 0.025 Om at film annealed at 1023 K, using the four probe Van der Pauw technique.

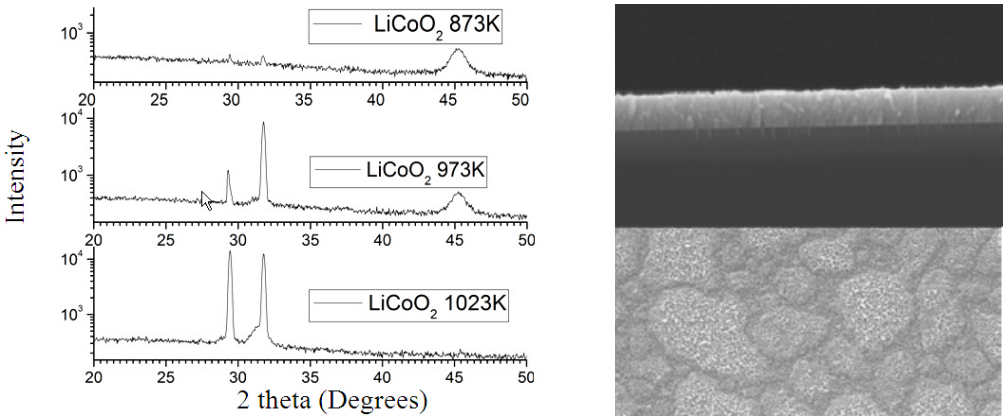

Fig. 3: On the left, X-ray diffraction patterns of $LiCoO_2$ after annealing at temperatures of 873 K, 973 K and 1023 K. On the right, SEM images (cross-sectional on top and surface on bottom) of $LiCoO_2$film annealed at 973 K.

The ionic conductivity of LiPON electrolyte film was measured with Nyquist diagram of impedance, performed at temperatures from 295 K to 315 K. Top and bottom Pt contacts were fabricated on LiPON films for ionic conductivity measurement (Fig. 4A). The LiPON 1 μm films were deposited on top of Al disc plates, with surface already covered with 100 nm of Pt to avoid unwanted reaction between the LiPON and the Al plate. On top of LiPON film, another 100 nm layer of Pt and 500 nm of Al protect LiPON films. The top Al plate was glued using silver conductive paint.

Table 1. Deposition parameters and measured ionic conductivity (s) of LiPON films

LiPON Film	RF Power (W)	N_2 (sccm)	Pressure (Pa)	s @ 295 K (Scm^{-1})	s @ 312 K (Scm^{-1})
#101	200	20	0.03	4×10^{-7}	9×10^{-7}
#102	200	20	0.7	2×10^{-7}	7×10^{-7}
#103	200	2	1	0.1×10^{-7}	0.5×10^{-7}

The real part of the impedance (Z') and the imaginary part (-Z'') was plotted (Fig. 4) from frequencies of 0.5 Hz to 65 kHz, considering a 25 mV sinusoidal input voltage. When the dashed lines in Nyquist diagram of impedance cross the x-axis, the conductance of the film is measured and conductivity calculated considering sample dimensions. The deposition pressure in LiPON depositions was correlated with ionic conductivity of LiPON (Table 1). The highest ionic conductivity (9×10-7 Scm-1) was achieved with a pressure of 0.03 Pa (film #101) at temperature of 312 K.

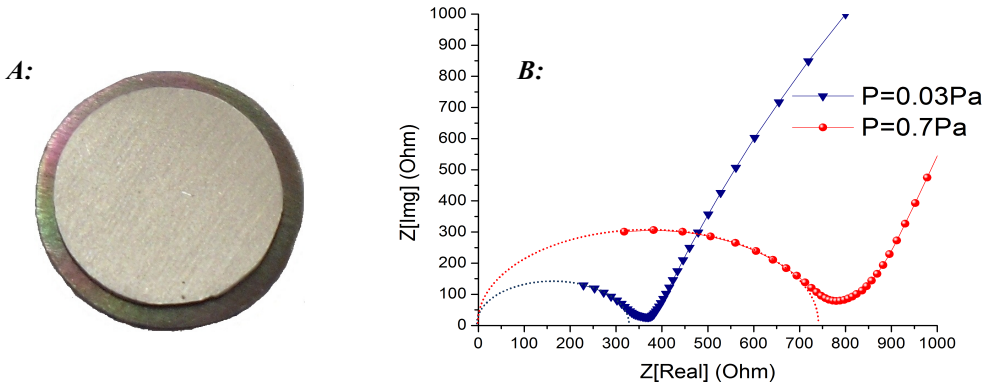

Fig.4: A - LiPON film with top and bottom contacts for ionic conductivity measurement. B - Nyquist diagram of LiPON films #101 and #102 measured at temperature of 295 K.

4. Conclusions

This paper presented the microfabrication and characterization of materials for thin-film solid-state rechargeable lithium batteries. The cathode is a lithium-cobalt oxide ($LiCoO_2$) film, deposited by reactive RF-sputtering at Ar/O_2 atmosphere. To obtain a good crystalline structure, annealing at temperature above 1000 K is recommended. The electrolyte is a glassy lithium-phosphorus oxynitride electrolyte (LiPON) film, also deposited by RF-reactive sputtering, at N_2 atmosphere. An ionic conductivity of 9×10^{-7} Scm^{-1} (by means of Nyquist diagrams) and an electronic resistivity greater than 10^{14} Ocm was measured at 312 K, The best LiPON films are deposited at low pressure (0.03 Pa) and low deposition rate. The lithium anode (3 µm) was deposited by thermal evaporation. The deposition of a protective layer is required before exposition to the air, due to the rapid oxidation of lithium. The platinum top contact layer and a subsequent Si_3N_4 film, deposited by low temperature hot-wire CVD, is proposed.

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